Parallel Implementation of Semiclassical Transition State Theory and its application to high-dimensional tunneling reactions

Chiara Aieta[a], Fabio Gabas[b], Michele Ceotto[c]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, chiara.aieta@unimi.it,*
[b] *Dipartimento di Chimica, Università degli Studi di Milano, fabio.gabas@unimi.it,*
[c] *Dipartimento di Chimica, Università degli Studi di Milano, michele.ceotto@unimi.it*

Semiclassical Transition State Theory (SCTST) can incorporate the non-separable coupling between degrees of freedom (DOFs) of reactive systems and include the effects of reaction path curvature and anharmonicity, as well as quantum tunneling contributions in the rate constant. The rate expression is derived by relying on a perturbative expansion for the vibrational energy which makes it possible to express the semiclassical cumulative reaction probability in a convenient way, without any further assumptions about the separability of the DOFs.[1-4]

The main goal of the talk is the extension of this semiclassical methodology to systems of increasing dimensionality upon computation of the densities of states for the reactants and the transition state by means of a convenient parallel implementation of the Wang-Landau algorithm.[5-6]

The new strategy is implemented into two codes, "paradensum" and "parsctst", which are currently distributed with the open source MultiWell program suite for chemical kinetics.[7] The needed input information is just the reaction barrier height, the normal mode frequencies, and the anharmonic force constants, which are routinely calculated by suitable electronic structure packages.

After describing the codes and demonstrating their computational accuracy and efficiency, the new implementation is applied to estimate the rate constant of the proton transfer isomerization of the 2,4,6-tri-*tert*-butylphenyl to 3,5-di-*tert*-butylneophyl, a reaction involving 145 degrees of freedom and showing a clear tunneling regime below 250K.[6]

References

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